奈良産業大学『産業と経済』第18巻第2号（2003年6月）157—184

Emergence of First Regenerated Cellulose Fiber Industry in the Late 19th Century: Chardonnet's Artificial Silk

Kenji Kamide

Synopsis: *An attempt was made to investigate a pre-history of emergence of chemical fiber industry. Socially widely prevailed tendency in late 19th century to produce high-value products by modifying chemically the naturally-occurred materials, which had been exclusively employed for low-value commodity, formed a strong incentive to invent new artificial materials such as cellulose nitrate. Existing industries were activated remarkably by replacing the natural materials with cellulose nitrate, which was then applied to bear new industries. Chemical fiber industry was a typical example. Numerous trials to produce artificial fiber from other materials than natural silk were historically surveyed mainly on the patent specifications. All the inventions, except Swan's, prior to Chardonnet's, were of 'Imagination Age'. Artificial thread was first produced temporarily on a small scale for electric incandescent lamp by carbonizing cellulose nitrate (to obtain carbon conductor). Electric lamp industry was a precursor of artificial industry. Five essential steps were noticed to be fulfilled concurrently to produce artificial silk for cloth or textiles. It was shown that all essential steps each had been invented, even though being far from perfection, separately by others than Chardonnet prior to Chardonnet's invention, which was commercialized on large scale for clothing. Chardonnet's process was consisted of cellulose nitrate, collodion, dry (or wet) spinning and after-treatment (denitration). In this sense, there was no significant originality in the principle of his process. However, Chardonnet's technology, judged from his patent specifications, was outstandingly precise and accurate enough to enable any one of average engineers or chemists to reproduce Chardonnet's invention by following the specification alone. Then, his patent specifications are equivalent or sometimes superior to contemporary scientific and technical papers. Chardonnet was the first, who used the term 'artificial silk' for the fibers spun from collodion. Chardonnet was also the first person, who applied his inventions internationally, and was the most productive: He had obtained 44 patents, which can be classified into 15 categories, ranging from 1884 to 1923 over almost 40 years (until one year before his death). These inventions had been commercialized worldwide by himself with financial help of investors. His predecessors each applied only single patent, which was not commercialized, to one country. Chardonnet studied at first in laboratory, then established a* *bench plant, which he operated for several years to accumulate know-how before commercialization. His development procedure is technologically very reasonable and now widely adopted in industry. Chardonnet's process evolved continuously even after commercialization.*

1 INTRODUCTION

The mechanization aiming for high productivity in the cotton fiber industry became the beginning of the industrial revolution in the end of 18^{th} century～the early 19^{th} century. Thereafter, electrical (communication) and inorganic and organic chemical industries had begun to rise since the middle of 19^{th} century. This time could be called as the 'second' industrial revolution in comparison with the 'first' industrial revolution. In the end of 19^{th} century chemical fibers had been attempted to be commercialized, based on the advanced technology at that time of the chemical industry. The chemical fiber industry thus emerged in that time developed quickly in the 20^{th} century to contemporary polymer chemical industries such as industries of, synthetic fibers and plastics. Unfortunately, any authoritative study on the worldwide history of emergence of artificial silk technology and its industry had not been published hitherto.

Chardonnet (Count Hilaire de Chardonnet or Count Hilaire Bernigaud de Chardonnet) is widely well known by his name as *'Father of Artificial Silk'*, but his real image is unclear. For examples, we cannot answer rightly to the following questions.

(1) What role did he play in chemical fiber industry?
(2) Who was he?, scientist?, inventor? or entrepreneur?
(3) Did he create first a concept of artificial silk?
(4) Was he the first man who invented the process of producing artificial silk?
(5) Did he materialize artificial silk?
(6) Was he mere inventor?
(7) Why had artificial silk been invented or produced in France, which was one of leading countries in natural silk production, together with Italy?
(8) Had artificial silk industry appeared by request of French silk industry?
(9) What happened to Chardonnet's silk and his industry?

Chardonnet's process does not exist any more, being extinct before starting of scientific research on cellulose and high polymers, which are the starting materials of the chemical fibers and the process is now an inheritance, which is an object of the historical study.

Up to now, several books[1-11] had been published on the artificial silk. But, these books are very fragmentary, being far from comprehensiveness and even contain a lot of mutual contradictions and did not cite the reference, in particular, the primary literature (with repetition of requotation and hearsay), in which author's description has ground, and did not give technical assessment to Chardonnet's inventions (if any).

This and subsequent articles attempt to give satisfactory answers to the above questions, by collecting carefully and comprehensively the most reliable historical evidences including, of course, the patent literature. Here, the following criterion is adopted for the research strategy;

(1) *The patent literature is the most reliable primary information.* Full specifications of patent literature of France, Germany, Britain, and USA are employed as absolute standard in any sense. For the survey, K. Süvern's book, a comprehensive collection of patents (sometimes, brief summary) on artificial silk during 1855~1925, is extremely valuable as the reference book.

(2) *Any author knows his mother country the best.* Therefore, the books of J. Foltzer,[1] A. Demoment,[2] and L. G. Fauquet[3] may be useful as standard.

(3) *Best author should be the person, who was engaged in textile at that time.* In this sense, Foltzer's book[1] is the best.

(2) and (3) can be quoted under the conditions that the descriptions in (2) and (3) do not contradict with those in (1). Books, which are not classified into the above three criterions, are regarded as less reliable. When there is mutual inconsistence, the more reliable book should be cited.

2 SOCIAL CIRCUMSTANCES AND SCIENCE OF MIDDLE 19^{TH} CENTURY IN EUROPE: NEW ERA OF SYNTHETIC MATERIALS

During 1830s~1850s the existence of cellulose, with chemical composition of $(C_6H_{12}O_5)_n$, on the earth glove was recognized as a fundamental component constituting plant issues. On the other hand, in 1840s~1850s for the effective application of dry-distillation residues of coal (coal tar) the development of medicines and artificial (synthetic) dyestuffs was made vigorously and as a result, organic chemistry advanced utterly concurrently and remarkably.[13,14] Approximately in this period, the industrial revolution, starting with mechanization of cotton fiber production→utilization of steam engines→metal machinery→transportation (turnpike road (before revolution)→water canal→railway), attained to the level of maturity.[15] Needless to say, the industrial revolution accelerated the advance of capitalism. Utilization of wood is a good example. Wood had been extensively employed only for construction of buildings and bridges-and ship-buildings and fuels. However, wood became in serious shortage in whole Britain due to massive usage of charcoal for iron-refining. Then, the iron-refining industry met the difficulty and import of iron from northern Europe became popular, until the cokes method was invented for iron-refining. The tar was the worthless bi-product in cokes production process.

Attempts of conversion of wood into the high-value added goods were undertaken: The first commercial success was paper manufacturing industry, which used wood pulp as starting material. J. P. Weibel,[16] the man, who financed until his death with his associates the commercialization of Chardonnet's invention of artificial silk, was a successor in wood pulp manufacture and paper making. Prince Guido Henckel von Donnersmarck,[17] an eminent German entrepreneur, who succeeded in paper manufacture, supported financially British ventures of viscose (C. F. Cross, E. J. Bevan and C. Beadle) and of regenerated cellulose fiber (C. H. Stearn and F. Topham).[18] In addition, Cross and Bevan were class mates and graduates of papermaking department of Owen's College at Manchester. The papermaking industry was in mid 19th century particularly prospered in Europe as a precursor of polymer chemical industry. And the capitalists of this industry were very keen to create from wood pulp more value-added-goods than paper.

In accord with progress of industrial revolution, especially explosive development of cotton fiber industry (1770～1840) massive demands for inorganic chemical compounds were formed in refining, finishing and dyeing processes, resulting in lowering of price of these chemicals by commercialization of new methods for production.[19] Under the above circumstances, study on the chemical reactions of cellulose became popular in 1830s～1850s. Chemical industry, whose development was induced by cotton fiber industry (mechanization of spinning process (1770～1800), and of weaving process (1830～1840)), became motives, in the next stage, of development of artificial fiber, which changed dramatically the constitution of fiber industry afterwards.

Cellulose nitrate, synthesized first in 1833, is the first artificial material, which emerged new industry such as man-made plastics industry and modern rayon industry, as illustrated in Fig. 1. Naturally-occurring materials, utilized so far in the traditional industries were replaced by cellulose nitrate (Table 1). The products had exhibited high performance and then its industry expanded quickly.

In addition, cellulose nitrate is readily soluble into various solvents to form gel or solution, which were used in the commercial processes. For example, until 1895 the following substances were known as solvents for cellulose nitrate[20]: (1) Essigsäure, allein order gemischt mit Alkohol order Äther, (2) Schwefelsäure, (3) Ätherschwefelsäure, (4) Aldehyde,

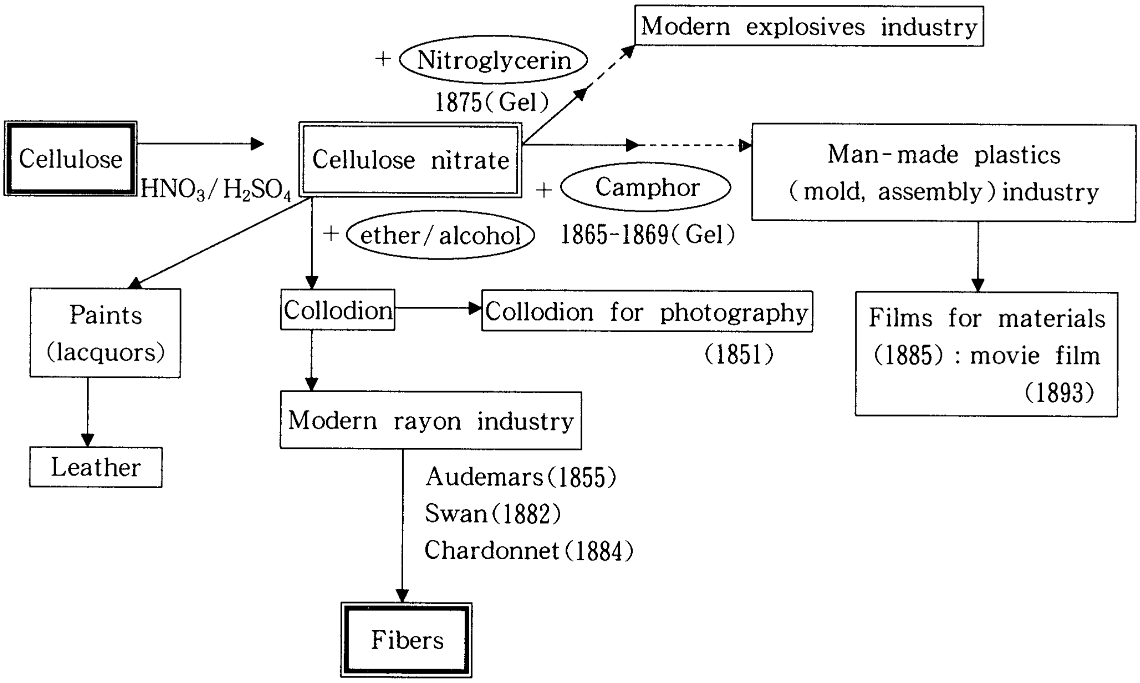

Figure 1 Genealogy of commercial applications of cellulose nitrate during 19th century

Table 1 Cellulose nitrate as new material in 19th century

Sector	Products used until emergence of cellulose nitrate	Cellulose nitrate products	Remarks
Explosives	gun powder	smokeless powder dynamite	modern explosives
Plastics	natural resin	celluloid (first artificial thermoplastics)	synthetic
Lacquer Coating	oil, natural resin	lacquer	modern paints
Fiber	silk	artificial silk	chemical fibers

Anilin, (5) Lösung von Kampfer in Alkohol, Äther, Benzol, Toluol order Tetrachlorkohlenstoff, (6) Essigäther, (7) Acetone, (8) Äther-alkohol, (9) Holzgeist (Methylalkohol), (10) Nitroglyzerin, (11) Nitrobenzol, (12) Amylacetate, (13) Verdünnte alkoholische Lösungen verschiedener Salze.

These characteristics (i. e., formability of gel and solutions) of cellulose nitrate had played a decisive role in creation of new industry. Then, it was rather a matter of course, that cellulose nitrate was chosen in the late 19th century as starting materials for production of man-made fibers; Regrettably no comprehensive historical survey on cellulose nitrate has been undertaken even in Europe, although the importance of cellulose nitrate in

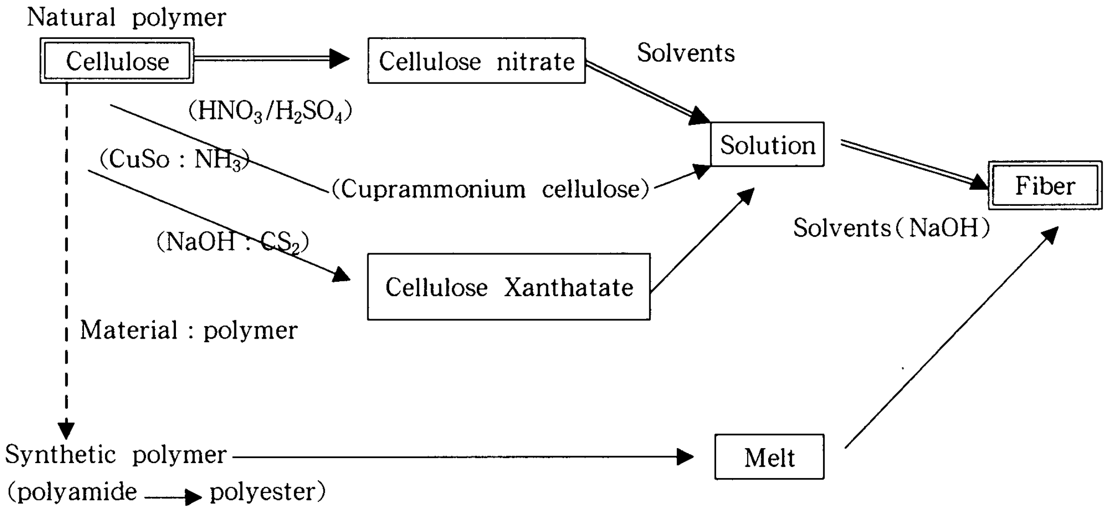

Figure 2 Evolution route of chemical fibers

Table 2 Nomenclature of starting substance employed for preparation of the spinning solutions, from which the fibers were produced

Year (AD)	Inventor	Name of starting substance	Reference
1882	E. Weston	pyroxyline; gun cotton; nitrocellulose	BP 4,458 (1882)[21]
1883	J. W. Swan	nitrocellulose	BP 5,978 (1883)[22]
1886	H. B. Chardonnet	pyroxyline	BP 2,211 (1886)[23]
1888	H. B. Chardonnet	pyroxyline	BP 5,270 (1888)[24]
1889	F. Lehner	nitrozellulose	BP 55,949 (1889)[25]
1890	H. B. Chardonnet	pyroxyline	BP 5,376 (1890)[26]
1891	F. Lehner	pyroxyline; nitro-cellulose; nitrated cellulose	BP 11,831 (1891)[27]
1894	F. Lehner	nitrozellulose	DP 82,555 (1894)[28]

BP, British Patent; DP, Deutsche Patent

the late 19th century～the early 20th century can never be underestimated.

Fig. 2 illustrates an evolution route of chemical fibers. Regenerated cellulose fiber from cellulose nitrate was the predecessor of chemical fibers. Here, it should not be misunderstood that industrial application of cellulose nitrate was attempted only after its physical and chemical properties had been exhaustively disclosed. Even in the period when the science of cellulose derivatives was not at all known, commercialization of the derivatives had been undertaken and as results attained by enormous efforts after repeated trials-and-errors some succeeded at least temporarily and a few are surviving until the present. Similar relations between industry and its related science can be found between synthetic dye (pharmaceutical) industry and organic chemistry in the second half of 19th century.

Name of cellulose nitrate was given to the reaction product of cellulose with nitric acid after it was experimentally confirmed that the reaction is not a nitration, but an esterification. The popularization of the name of 'cellulose nitrate' occurred far after the experimental confirmation. Until that time, in the whole period of invention of artificial silk, the reaction products had been erroneously identified as nitro compound. Table 2 collects the names of starting materials employed in the patent specifications.

3 IDEA OF ARTIFICIAL SILK BEFORE CHARDONNET'S METHOD

Before Chardonnet invented artificial silk many persons had dreamed artificial silk and practically studied or even produced small piece of artificial silk. Robert Hook, British physicist (1635~1703) stated, in the book *'Micrographia'* (Observe V), published in 1644 (at his age of 29), in which he sketched numerous living things with astonishing precise and accuracy using high performance micrograph constructed by himself, that *'probably there might be a way found out, to make an artificial glutinous composition······. If such a composition were found, it were······an easie matter to found very quick ways of drawing it out into small wires for use'.*[29]

Since then (1735), Rene A. F. Reaumur, French physicist and naturalist (1683~1757) repeated the same idea as Hook in *'Memoires pour server â e'histoire des insects'.*[30,31] The details of his idea can be found in the literature[30,31]: He described *'Silk is only a liquid gum which has been dried. Could we not make silk ourselves with gums and resins?* (English translation). George Audemars of Lausanne (Swiss) obtained British Patent No. 283 (1855) under the title of 'Obtaining and Treating Vegetable Fibres'. The fibers separated from the inner bark of mulberry tree and other trees of the genus morus are converted into an explosive compound by the action of nitric acid, and then dissolved in a mixture of alcohol and ether (used in equal proportion), in which then mixed with a solution of caoutchouc. Into the mixture thus prepared a steel point is dipped, and thus a thread is drawn from the surface of the liquid; this thread is connected with a winding machine, by which it is drawn out until the liquid is exhausted. The thread thus obtained is worked in the same manner as may be used as substitute for silk. This patent may be the first artificial silk, as a substitute for silk, from cellulose. Note that Audemars had not used a terminology *'Artificial Silk'* in his patent specification.

In the late 19th century, with development of electric lamp industry attempts were made to carbonize cellulose nitrate fiber to give carbon conductor for incandescent electric lamp.

Here, starting material of carbon conductors for electric lamp advanced in the following way: Paper tape→perchmented cotton→denitrated collodion fiber. Edward Weston, a British living at Newark, New Jersey, USA at the time when he applied patent (British Patent No. 4458 (1882)),[21] invented the method for production of carbon conductor: Cellulose (cotton, cotton waste, linen or paper) was subjected to the action of a mixture of nitric and sulphuric acids to yield the substance, commonly known as pyroxyline, gun cotton or nitrocellulose. By dissolving this substance with a mixture of ether and alcohol, collodion was produced. Collodion was formed in thin sheets and dried. The sheets were treated with reducing or de-oxidizing agents, such as ammonium sulphide, protochloride of iron, to convert pyroxyline to cellulose, which was finally carbonized. His invention had not been commercialized. Next, Joseph Wilson, a British chemist (1828～1914) (since 1904, Sir) invented the method for production of carbon filaments possessing perfectly uniform sectional size and at the same time homogeneous and uniform in size.[22] He produced fiber by dissolving cellulose nitrate (nitrocellulose) into glacial acetic acid and squeezing or extracting under pressure the solution thus prepared through hole and denitrating (de-esterfying) the fibers with de-oxidizing agent (hydrosulphate of ammonia or others) and subsequently carbonizing the resulting filaments.

Now, it is evident that in the production of artificial silk (chemical fiber) as a substitute of natural silk, the following five essentials (i. e., elementary steps) should be materialized, at least to some extent[14,32] (Fig. 3):

(1) *Chemical conversion* of natural polymer to a derivative which is soluble in solvents [conversion of cellulose to cellulose nitrate].

(2) *Preparation of solution* by dissolving the derivative into the solvent or solvent mixture [solution of cellulose nitrate in a mixture of ether (diethylether) and alcohol

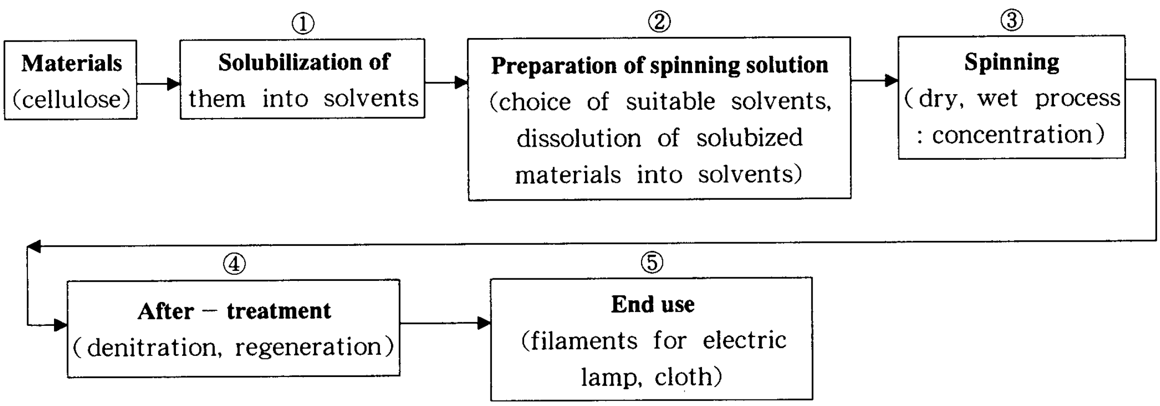

Figure 3 Five major essentials for production of artificial silk

(methanol)].

(3) *Spinning* of fibers from the solution.

(4) *After-treatment* of the fibers, if necessary [de-esterification for stabilization].

(5) *Utilization* of the treated fibers for use of specific area [clothing].

Here, bracket means Chardonnet's claim.

Before Chardonnet invented the process for producing artificial silk in 1884, the major requisites had been fully investigated:

(1) Cellulose nitrate was first synthesized by H. Braconnet in 1833[33,34]: He obtained white inflammable powders by action of concentrated nitric acid on cotton, sawdust of wood and paper and named the powder 'Xyloidines'. C. F. Schönbein, German professor of chemistry in Basel University, synthesized in 1845 gun cotton by reacting pure cellulose with potassium nitrate and sulfuric acid.[35,36] The manufacture of a nitrated material from cotton by treating it with a mixture of nitric acid and sulfuric acid was patented by him in 1846. The gun cotton factory had seriously exploded in Faversham in 1847.[36]

(2) In 1847 or 1846 Louis Menard (Maynard), égalemeut, le peitre, poëte and chemist, discovered with collaboration of Flores Domonte that cellulose nitrate dissolves readily into a mixture of ether and alcohol, which was called as 'Collodion'.[37]

(3) In 1842 Louis Schwabe, manufacturer of silk fabric of Manchester, invented and patented the process of spinning of the filament through die.[38] Afterwards (1862), Ozanam proposed the same idea.[37,39]

(4) As mentioned before Audemars employed in 1855 stabilization treatment for cellulose nitrate fibers in order to control the carbonization rate.[40] Swan also de-esterified the fiber for the same purpose (1883).

4 Le Hilaire Conte Bernigaud de Chardonnet de Grange (H. de Chardonnet)

Chardonnet is sometimes memorized as 'the person who had invented artificial silk first in the world'. But, this statement is very inaccurate as is evident in the preceding section. Chardonnet was (a) scientist, who had received higher education, (b) outstanding engineer, who had commercialized his achievements of research, and (c) entrepreneur, who had, even though temporarily, succeeded economically.

His personal character can be expressed as: curious noble inventor; passionate royalist; man, who had a continued ardor for invention for more than 40 years. W. E. Wicht[41] wrote that Chardonnet was 'beschäftigte sich mit weitgespannten biologischen, physikalischen und technischen Interessen wissenschaftlichen und praktisch'. C. F. Cross, one of the inventors of viscose and viscose rayon commented that Chardonnet was *'purposeful inventor equipped with the training of the Ecole Polytechnic'*.[42]

Chardonnet was born in 1839 (1st May) at Besançon in east France[43] and died in 1924 (11th March) at Paris.[41,44] He received primary education directly from his father, who was an amateur scientist, and after that he learnt mechanical engineering, physics and chemistry at Faculté des Sciences located at Besançon, belonging to the local academy of sciences at that time. His chemistry professor was a brother-in law of L. Pasteur.[42,45] Chardonnet entered in 1859 (at his age of 20) Ecole Impérial Polytechnique at Paris, graduated in 1861 with first honorary degree. He was an academic stuff there, but soon was forced te resign, because he rejected to take a pledge, asked by Napoléon III for all governmental officers on May, 1861.[45] Since then Chardonnet had never entered governmental service again. In 1865 (26 years old) he got married to Mell. de Roulz.[45] It was erroneously said that while a student at the Ecole, Chardonnet was a student under L. Pasteur (1822～1895) who was at that time engaged in study of the diseases of silk worm (Pébrine investigation).[46-48] Note that L. Pasteur was professor at Strasburg University in 1848, moved to Lille University in 1854. During 1857～67 Pasteur was professor at Ecole de Beaux-Arts, where he was entrusted the study on small particle (virus)disease of silk worm in 1865. Afterward (1867) he took a chair of Université de Paris.[49,50] Pasteur had never taken the position at Ecole Polytechnique.

Since it is evident that Chardonnet worked under Pasteur studying silk worm, Chardonnet's study was carried out at least after 1865. He graduated from the Ecole already 4 years before. Chardonnet is considered to have started research under guidance of Pasteur in 1865～1866. However, Chardonnet was soon aware that he was keenly attracted in silk fabrics rather than silk worm, getting an idea of producing artificial silk.[45] Demoment wrote on these circumstances[51] : *'L'idée d'obtenir un jour un fil artificiel lui est venue en 1865～1866, nous l'avons dit, alors qu'il se livrait à l'étude demandée par le comte de Chambord sur la maladie des vers à soie et observait, d'un oeil attentif le travail du bombyx'*.

Chardonnet had noticed that collodion had good spinnability and the liquid flew out from the bottle showed beautiful luster resembling natural silk when dried. Note that he was for long very familiar with collodion, which was daily used for photographic dry plate.[52] More concrete idea of producing artificial silk came to Chardonnet in 1878[45] : *'Vers 1878, cette idée prend corps, peut-être à la suite d'um petit incident qui est devenu légendaire: un soir dans le laboratoire de ce chercheur, sa femme de ménage renverse un flacon de collodion, c'est-à-dire de la nitro-cellulose dissolute dans l'éther. De la table, le collodion coule jusqu' à terre en* *un mince filet, et le lendemain matin, quand Chardonnet entre dans la piēce, il aperçoit, reliant la table ã la terre, un magnifique fil brillant comme de la soie. Au bout de ses doigts, se forme un fil de collodion, et enthousiamē, il pense qu'il a trouvē sa voie.*

5 Chardonnet's inventions of artificial silk: His first and second patents

Fig. 4 illustrates the chronological chart of Chardonnet's work.

In 1878 Chardonnet built *petit atelier* at Chateau de Vernay-de-Charette, Besançon, Duob, France,[52] where he devoted to developmental study of production of artificial silk from the collodion (Phase I). At the atelier he had a precise spinning apparatus (single spinneret type) until 1884 and the apparatus was progressed upto 12 spinneret type. Phase I corresponds to a bench-scale development laboratory. The atelier was operated until about July, 1893.

Who had named the fibers produced from collodion solution or similar solutions 'artificial silk' (soies artificielles or Künstliche Seide (Künstseide))? Table 3 collects the nomenclature given to the fibers artificially spun from collodion in the patent literature. It is evident from the table that Chardonnet named as early as 1884 the above fibers artificial silk. According to Hard, Joseph Wilson Swan exhibited in Inventions Exhibitions in 1885 mata and d'oyleys, croched by the thread produced according to Btitish Patent (No. 5,978 (1883)), under description 'artificial silk'.[60] Süvern described that *'Nach einer Notiz im Journal of the Society of Chemistry 1885, Vol. 15, p34 sind diese Faeden such als 'Künstliche Seide' bezieichnet warden'* (*by Swan*).[61]

On 9 May, 1884 Chardonnet deposited the documents, in which the results of his researches were written, sealed to Academie des Sciences de Paris. Several literature disclose this as follows:

(1) *Au printemps de 1884, M. Ěmile Blanchard, membre de l'Insitut, reprend une idēe qui lui est chēre depuis 1865 et fait ã l'Acadēmie des Sciences une communication sur la possibilitē de produire soie par des moyens artificiels. Son idēe est alors dejã rēalisēe. En effect, quelque jours aprēs le 12 mai de cette annēe 1884, Chardonnet dēpose ã la même Acadēmie (Acadēmie des Sciences) un pli cachetē. Le 7 novembre 1887 seulement sera ouverte, ã la demande de l'inventeur, cette vēritable charte de la soie artificielle qu'il insititute loyalement; Sur une matiēr textile artificielle ressemblant ã la soie.*[62]

(2) *La 9 mai 1884, il (Chardonnet) dēpose ã l'Acadēmie des Sciences de Paris un pli cachetē rēnfermat les rēsultats de ses premiēres arnēes d'ētude.*[63]

(3) *1884 hinterlegte er (Chardonnet) das Ergebnis seiner Forschungsarbeit verschlossen bei*

1861	Graduation from Ecole Politechnique
1865	Biological research : idea of artificial silk under L. Pasteur
1878	Start of research on artificial silk
1884	First Patent FP No. 165, 349 (BP No. 6, 045 (1985)) (method)
1885	Second Patent FP No. 172, 207 (BP No. 2, 211 (1886)) (method and apparatus) (six spinnert machine)
1889	Expo { FP No. 199, 494 (BP No. 5, 270 ('89) : DP Nr. 46, 125) FP No. 201, 740 (BP No. 656 ('89) : DP Nr. 56, 331) (12 spin. machine, 4 fil~6 fil/fiber)
1890	Company { FP No. 203, 202 FP No. 207, 624 (BP No. 5, 376 (1890)) FP No. 208, 405
1891	{ FP No. 216, 156 FP No. 216, 564
1892	Start of production { FP No. 221, 488 FP No. 225, 567
1893	FP No. 231, 230
1894	Suspension of production DP Nr. 81, 599 BP No. 24, 638 Re-opening DP Nr. 82, 555
1900	
1910	

Figure 4 Chronological chart of Chardonnet's work

Table 3 Who was the first to name new fibers, spun from collodion, 'Artificial Silk'?

Year (AD)	Inventor	Usage of artificial silk	Remarks
1855	G. Audemas	X (thread, vegitable fiber)	BP No. 283 (1855)[40]
1882	E. Weston	X (thread)	BP No. 4,458 (1882)[21]
1883	J. W. Swan	X (filament, thread)	BP No. 5,978 (1883)[22]
1884	H. Chardonnet	O (soie artificielle)	FP No. 165,349 (1884)[53]
1885	H Chardonnet	O (Kunst Seide)	DP Nr. 38,368 (1885)[54]
1886	M. P. E. Gerad	X (Fäden)	DP Nr. 40,373 (1886)[55]
1889	Lehner	O (Kunstlicher Seide)	DP Nr. 55,949 (1889)[56]
1889	J. H. duVivier	O (Kunstlicher Seide)	DP Nr. 52,977 (1889)[57]
1890	H. Chardonnet	O	BP No. 1,656 (1890)[58]
1891	H. Chardonnet	O	US P No. 460,629 (1891)[59]

X: inventor did not name new fiber artificial silk
O: inventor named new fiber artificial silk.
Parenthesis shows words which were adopted in the patent specifications to indicate new fibers.

der Akademie der Wissenschaften in Paris.[64]

(4) *In France, count Hilaire de Chardonnet evolved a virtually identical process, details of which he had deposited with the Academie des Sciences in May 1884……*.[65]

(5) *In 1884 Chardonnet reported absolutely the same process to the society……*.[66,67] (tanslated from Japanese)

(6) *Hilaire de Chardonnet invented the method of producing continuous filaments and wrote a paper, entitled (Les soies artificielles), which was presented to the academy of sciences under the conditions that it should be opened three years after. On 7 November 1887 this paper was opened and made public* (translated from Japanese).[68]

Chardonnet's first patent, entitled *'Fabrication des Soies artificielles par la filat liquid'*, was registered on 17 November, 1884 (France Patent No. 165,349).[69] To the original specification, amendments were made twice on 10 December 1884 and on 7 May 1885.[70]

Table 4 collects the literature information on the date of registration of Chardonnet's first patent. Surprisingly, among 9 books only two French and one German books described the correct date, although even these two French books did not mention the amendment of the patent. Note that Süvern's book is just a compilation of the patents.

In the first patent what Chardonnet claimed (Patent Anspruch) was: The method for production of artificial silk by forcing through a hole the solution of cellulose nitrate (pyroxyline) in ether～alcohol mixture (to which small amount of metallic chloride and oxidative organic salt are added) and coagulating the extrudate in water and drawing it

Table 4 Chardonnet's first patent (French Patent No. 1,653,459)

Year of file	Reference	Remarks
1883	Koeningberger[71]	
1884	Reinthaler[72]	
1884 (12 May)	Hard[73]	
1884 (17 Nov.)	Fauquet[74]	O
1884 (17 Nov.)	Demoment[75]	O
1884 (17 Nov.)	Suevern[76]	O
1885	Coleman[77]	
1885	Yamazaki[78]	
1885	Yamazaki[79]	

O: true description

(in the improved method, in air for drawing).

The Chardonnet's artificial silk had progressed from Stage I to Stage III as follows:

Stage I : Wet-spinning/non-denitration method

Stage II ; Dry-spinning/non-denitration method

Stage III: Wet-or dry-spinning/denitration method.

More detailed discussion will be given to Stages II and III in the forthcoming paper.

Almost the same inventions as France Patent No. 165,349 (1884) had been applied to Britain (British Patent No. 6,045 (1885)) and Germany (Deutsche Patent Nr. 38,368 (Kl 29) (1885)), simultaneously. Photograph 1 shows the first page of the Deutsche Patent Nr. 38,368 (1885).

Table 5 collects the list of all the Chardonnet's patents, licensed in his whole life-long, on artificial silk. The patents with the same content of specifications are located on the same line of the table. Chardonnet made inventions of totally 15 categories. Note that the patents located on the same line of Table 5 are not always absolutely identical with each other. For examples, in No. 3 category the spinning pressure was specified as 10 to 12 atmospheric pressure (atm) in British Patent No. 1,656 (1890) and 6~12 atm in US Patent No. 460,629 (1891) and in No. 6 category the nitrating conditions were different between British Patent No. 5,376 (1890) and US Patent No. 455,245 (1891) (see, Table 7, B (1) and B (1)'). Chardonnet had applied his last invention one year before his death. Then, it is clear that he devoted his whole life to the artificial silk technology.

The second invention is France Patent No. 172,207 (1885), which is related to improvement of the first patent and the manufacturing apparatus. The patent contains six precise

Table 5 Chardonnet's patents on artificial silk

No.	France Patent No.	British Patent No	Deutsche Patent Nr.	US Patent No.
1	165,349(1884)*a	6,045(1885)*b	38,368(1885)	394,559(1885)
2	172,207(1885)	2,211(1886)		
3	199,494(1889)	1,656(1890)	56,331(1890)	460,629(1891)
4	201,740(1889)	5,270(1888)	46,125(1888)	
5	203,202(1890)			
6	207,624(1890)	5,376(1890)	56,655(1890)	455,245(1891)
7	208,405(1890)	19,560(1891)	64,031(1891)	
8	216,156(1891)			
9	221,488(1892)			
10	225,567(1892)			
11	231,230(1893)	24,638(1893)	81,599(1893)	531,158(1894)
12	478,404(1915)	10,858(1915)	327,323(1915)	
13	478,405(1915)	10,857(1915)	320,908(1915)	
14	554,195(1922)			
15	563,682(1923)			

*a: France patent did not have its second year tax paid and therefore only bibliographic details were published and not a full specification.
*b: The application was abandoned before the publication.

Table 5 Chardonnet's patents (continued)

No.	Contents of the invention
1	O : First invention (1884)
2	O : Second invention (1885)
3	O : Improvements on the process and apparatus (1889)
4	Partial denitration (1889)
5	······
6	O : Nitration and denitration (1890)
7	Drying of cellulose at higher temperature (150～170℃) (1891)
8	Machine (1891)
9	Denitrating reagents (1892): Kalzium momosufür, Kalzium sulhydrat
10	······
11	O : Detailed description of the improved process (1893); moist pyroxyline; wet (water)-and dry (air)-spinning; denitration
12	······
13	Maschine zum Verspinnen von Kollodium (1915)
14	Regel vorrichtung für die Zuführung des Kollodiumspinnmaschinen (1922)
15	Vorrichtung für Kunstseidenspinnmaschinen zum Verteil des Kollodium (1923)

O; important invention

drawings of the spinning machines. This means that Chardonnet had undertaken at least the construction of the machines and had performed the test operation for a good while.

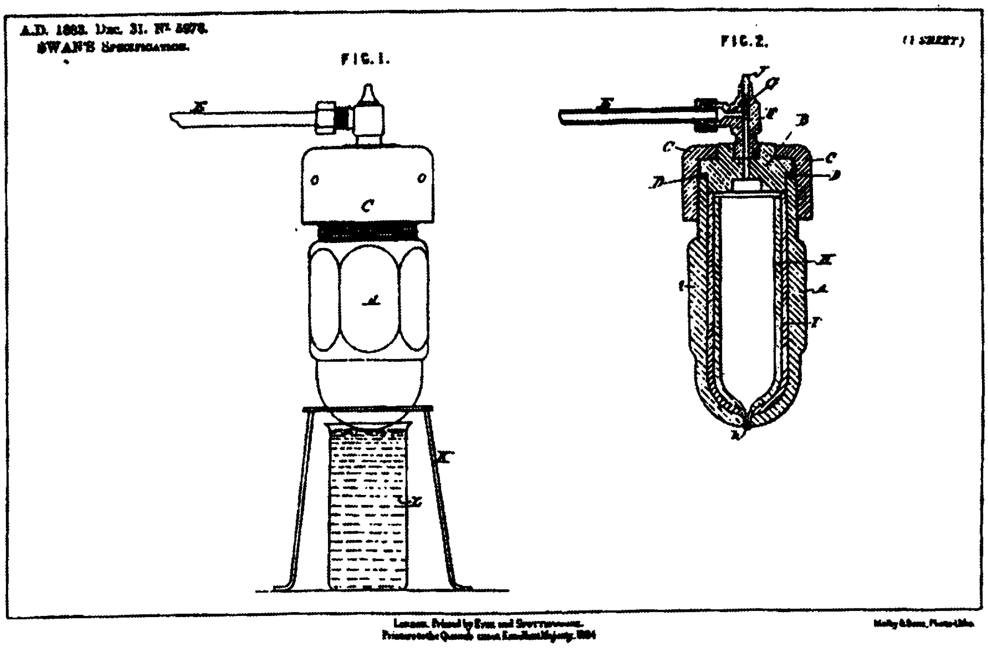

Figure 5 Swan's spinning portion
(Fig. 1 in British Patent No. 5,978 of 1883) (ref. 22)

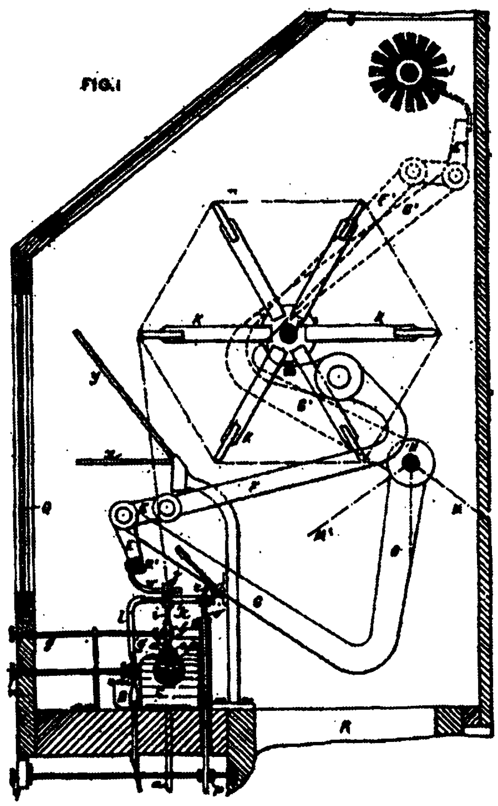

Figure 6 Chardonnet's spinning machine
(Fig. 1 in British patent No. 2.211 of 1886) (ref. 23)

In addition, in the later inventions, for example, France Patent No. 201,740 (1889), the detailed figures of real-size spinning machine with 12 dies were illustrated. In this case, four or six filaments were bundled into a yarn, which was the first multifilament artificial fibers.

Figs. 5 and 6 illustrate Swan's spinning portion (cited from Fig. 1 of British Patent No. 5,978 (1883)) and Chardonnet's spinning machine (from Fig. 1 of British Patent No. 2,211 (1886)), respectively. From the comparison of these two figures we can realize that the former is only a primitive simple tool and the latter is really a precision machine, implying that difference in the level of actual development between Chardonnet and his predecessors such as Swan is tremendously large. Without actual experience of plant operations such a complete specification with precise machines drawings could not be written. The specifications of the first and second inventions had come up to high standard.

Table 6 summarizes the experimental conditions, including temperature, pressure, concentration, and time, and the number of drawings described in the typical patents of artificial silk registered during 1855 and 1891. It becomes clear that in the patents filed in 1855

Table 6 Transition of 'Imagination Age' to 'Realization with Technology Age' in history of chemical fiber

Year	Inventor	Experimental conditions (in the specification)	Number of drawings
1855	Audemas[40]	no	0
1882	Weston[21]	no	0
1883	Swan[22]	a liquid such as alcohol (of say from seventy to eighty percent of spirit)	2
1886	Chardonnet[23]	conc. of reducing reagents; diameter of die (1/10mm): composition of collodion: pressure (2~3 atm)	6
1889	Lehner[25]	···schüttelt man 500g fein gepulventen Kopal order Sandarak mit 2400g Äthen···	1
1890	Chardonnet[58]	a mixture of 40 percent of ether and 60 percent of alcohol in volume: pressure (10~12 atm): apparatus	8
1890	Chardonnet[26]	nitric acid of 36°Be from 30° to 35℃ in a few hours: 6% of nitrogen	1 (BP No. 5,376)
1891	Chardonnet[59]	pressure (6~12 atm)	(USP No. 460,629)
1981	Chardonnet[59]	apparatus	14

and 1882 no detailed conditions were specified and no figure was shown, indicating that the specification is rather vague and can not be reproduced according to the patent specification alone. In contrast to.this, Chardonnet's patents specified the experimental conditions in very strict manner and his inventions can be reasonably reproduced according to the specification. His patents also contain numerous precise drawings. Then, Chardonnet's patents can be regarded to be almost equivalent to or sometimes superior to the contemporary scientific papers and patents. Swan's patent lied at intermediate step. He specified only the concentration of coagulant and illustrated two simple figures. We can conclude that as far as the artificial silk industry is concerned, the time before 1855 is 'Imagination Age' and 'Realization Age' started from 1884.

Fig. 7 shows the manufacturing process and apparatus for the production of artificial silk and the recovery of waste solutions, based on Chardonnet's original invention (British Patent No. 1,656 (1890)). It is interesting to see that Chardonnet realized the commercial importance of solvent recovery to reduce the production cost. Afterwards, the Chardonnet's companies applied the process of solvent recovery, which had been established in Phase I at the atlier.

Fig. 8 shows the improved process of Chardonnet's silk (British Patent No. 24,638 (1893), Deutsche Patent Nr. 231,230 (1893) and US Patent No. 531,158 (1894)), which had been invented, probably, at the commercial plant in Phase II and Phase III.

Table 7 summarizes the manufacturing conditions of artificial silk. The table was constructed on the basis of the specifications of the patents (Table 5). It is evident that Chardonnet process grew and progressed continuously even after the commercialization. Therefore, we cannot understand thoroughly the Chardonnet's process only from the first and second patents, which are target of this article. Chardonnet's technology is a great congregation of his patents and know-how, whose content was changed always, although its rate might be diminished with time.

Following additional remarks can be made to Table 7:

(1) The raw material which Chardonnet had started with was said to be mulberry leaf, since this was the natural food of silk worm,[88] or to be mulberry fiber.[89] However, any documentary primary evidence to support the above statements was not found. Needless to say, the reasoning of usage of mulberry is scientifically nonsense.

(2) Relationships between the nitrogen content (N%) of cellulose nitrate and the solubility into ether-alcohol (2: 1 in volume), established by Will in 1902 indicate that cellulose nitrate with $N=10.5\sim12.6\%$ is soluble in the mixture (the solubility$=95\pm5\%$).[90] Fig. 9 is

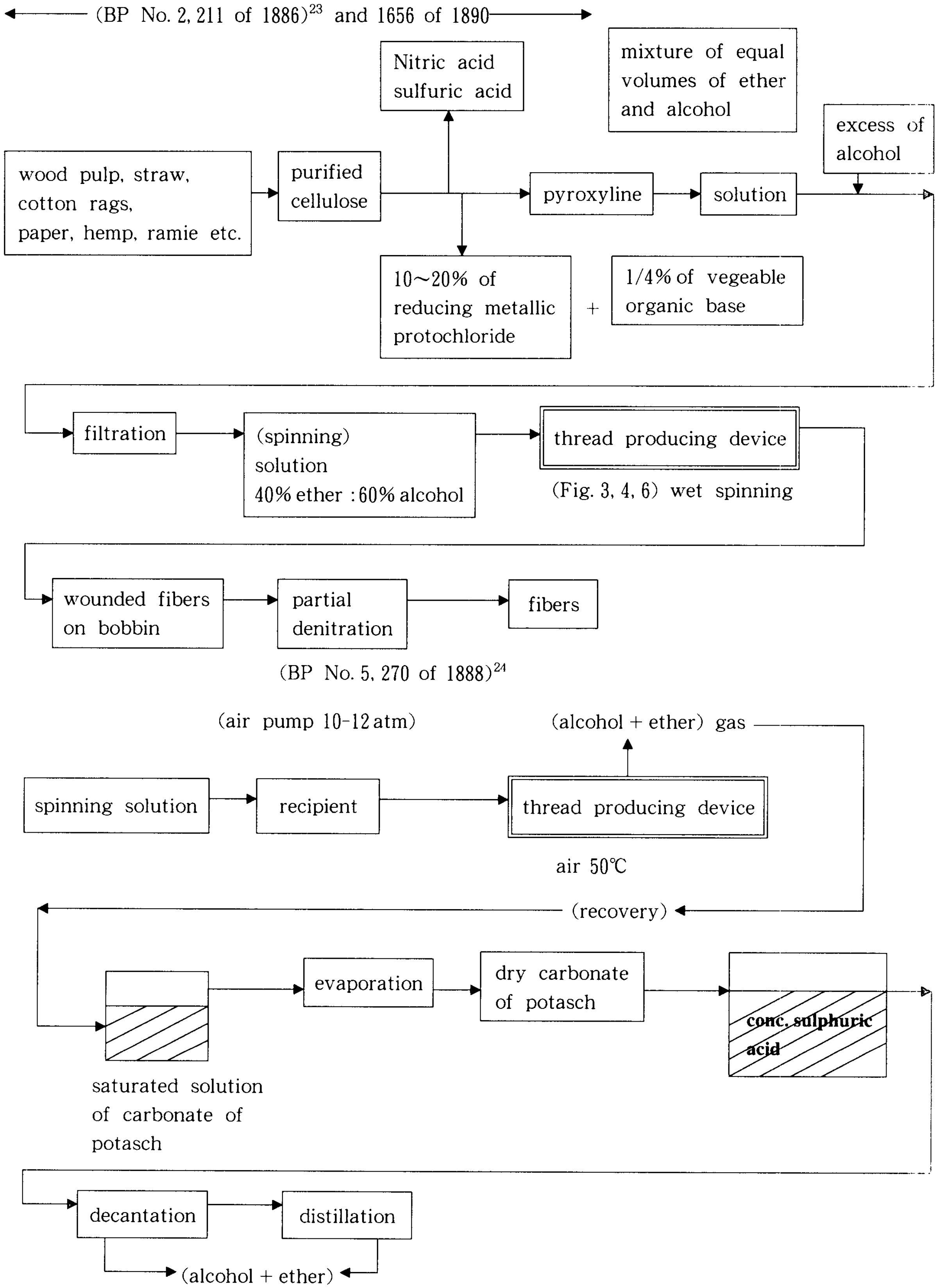

Figure 7 Manufacture and apparatus of artificial silk filaments (Chardonnet's original process : BP No. 1, 656(1890)[58]

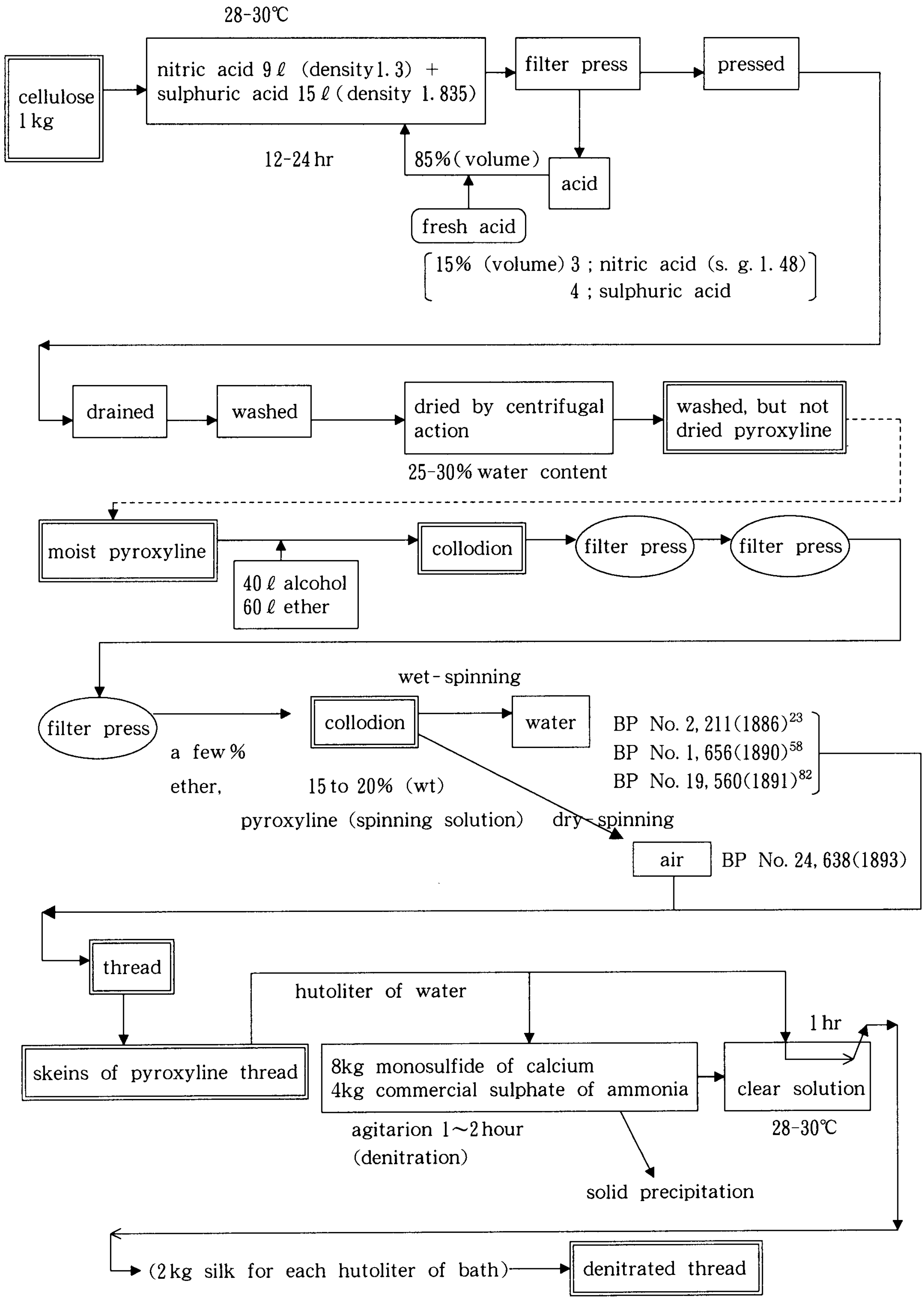

Figure 8 Improved process of Chardonnet's silk

Table 7 Manufacturing conditions of Chardonnet's silk

Items	Specifications	Reference
A. Cellulose :		
(1)	Gereinigte Zellulose aus Holzstoff, Stroh-papierzeug, Baumwolle, Lumnen, Filterpapier, Hauf, Ramie	(DP Nr. 56,331 (1890))[80]
(2)	Cellulose properly purified	(BP No. 1,656 (1890))[58]
(3)	Cotton fiber or any other cellulose (ramie, hemp, purified wood pulp, rags, etc)	(USP No. 455,245 (1891))[81]
(4)	Heat during 6 to 8 hours continuously at constant temperature, from 150 to 170℃, to cellulose materials, wood, cotton, ramie etc (to improve the purity and the solubility of cellulose nitrate).	(BP No. 19,560 (1891))[82]
B. Cellulose nitrate :		
(1)	Nitration (1890); Steeping cellulose in a suitable mixture of sulphuric acid and nitric acid (for example, 12 litres of nitric acid of the density of 1.37 and 20 litres of sulphuric acid of the density of 1.83). No. 6 of Table 5	(BP No. 5,376 (1890))[26]
(2)	Nitration (1891); to 1 kg of dry cotton use 12 *l* of nitric acid at the density of 1.34 and 18 *l* of sulphuric acid at the density of 1.83. No. 6	(USP No. 455,245 (1891))[83]
(3)	Nitration (1893); 1 kilo of cellulose is soaked in a mixture of 9 litres nitric acid of density 1.3, and 15 litres sulphuric acid of density 1.835, the whole at temperature of 28° to 30℃. The reaction is allowed to go on for 12 to 24 hours.	(BP No. 24,638 (1893))[84]
(4)	Nitration (1890); The cellulose was properly purified and nitrated in the usual way.	No. 3 (BP No. 1,656 (1890))[58]
(5)	Dry (i. e., vollstaendige Trocknen) pyroxyline.	No. 1, No. 3
(6)	Pyroxyline containing water (water content<20～30%)	No. 11
C. Composition of solution :		
(1)	1884～1885 : 40% of ether and 60% of alcohol.	No. 1
(2)	1889～1891 : equal amount of ether and alcohol+alcohol of about half volume thereof first employed.	No. 3
(3)	1893～ : 60% of ether and 40% of alcohol.	No. 11
D. Third components in the solution :		
(1)	1884 : Reducing metallic protochloride (Fe, Cr, Mg, Zn). 10～20g to 100g of pyroxyline	No. 1
(2)	1889 : Organic oxidisable base (chinin, aniline, rosanilin), 0.2g to 100g of pyroxyline	No. 3
(3)	1893 : nothing	No. 11
E. Dissolving procedure :		

Mixture of equal volumes of ether and alcohol, to which is afterwards added excess of alcohol to the extent of about half the volume thereof first employed; 1: (1+1/2) = 0.4: 0.6 No. 3

F. Polymer concentration :

(1) 1884 : 2~3% (3g pyroxyline in 100~150cc ether/alcohol mixture)*a.

(2) 1885 : 2~5% (100g pyroxyline in 2~5 *l* eines Gemisches von 40% Äether und 60% Alkohol) No. 1

(3) 2% Fauquet, p 101[85]

(4) 1893 : 20~22.5% [(28~30)×(0.7~0.75)] No. 11

(5) 1894 : >15~20% USP No. 531,158 (1894)[86]

G. Spinning method :

(1) 1884 : Dry spinning (air) No. 2

(2) 1889 : Wet spinning (water) No. 3

(3) 1893 : Dry spinning (air) No. 11

H. Spinning : nozzle diameter

1884 : 1/20 to 1/5mm No. 123

[1/4 to 1/2mm; Lehner BP No. 11,831 (1891)[27], DP Nr. 82,555 (1894)[28]]

I. Spinning : pressure

1885 : 2~3 atm No. 2

1889 : 10~12 atm BP No. 1,656 (1890)[58]

modern process : 60kg/cm^2 Foltzer, p23[87]

J. Denitration :

1888 : The pyroxyline is maintained at a temperature of 35℃ in a bath of nitric acid of a density of about 1.82. In a few hours it loses part of its nitrogen and reaches a condition below that of tetranitric cellulose (M. Vieille). The process when apllied to artificial silk (spun collodion) renders it unnecessary to introduce into the mother solution metallic chloride or alkaloids for lessening combustibility. BP No. 5,270 (1888)[24]

1893 : 8 kilos. of calcium monosulphide (or equivalent quantity of hydrosulphate of calcium sulphide, soda ash) and 4 kilos. of commercial ammonium sulphate (or equivalent quantity of as ammonium nitrate or hydrochlorate or other ammoniacal salt) are introduced into a hectolitere of water, in which 2 kilos. of silk is treated at 28° or 30℃ for about an hour. No. 11

*a: Deposited document at Science Academie in 1884

the plot of the solubility against N% of cellulose nitrate in the mixture of ether-alcohol, reproduced from ref. 90. Then, cellulose nitrate employed for production of artificial silk

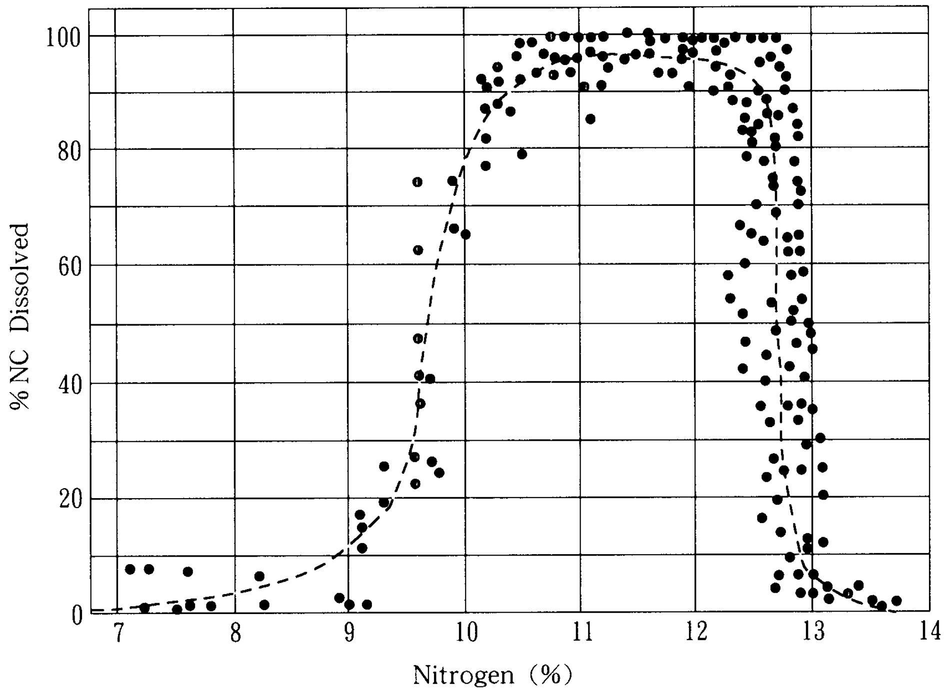

Figure 9 Nitrogen content and solubility in ether-alcohol(2-1)(Will)(ref. 90)

can be regarded as commercial grade cellulose nitrate. Chardonnet demonstrated an example of a pyroxyline having about 12% of nitrogen in (provisional and complete) specifications of British Patent No. 5,376 (1890). Chardonnet discovered that pyroxyline containing water was made easily soluble in ether-alcohol than the dry product (see, Table 7 B (4)). In addition, the spinning solution thus prepared is not very combustible (compared with that from the dry product) and is suitable for the dry spinning.[91]

(3) The nozzles consist of a glass tube terminating at the upper end in a contracted orifice of 1/20 th to 1/5 th millimeter in diameter.[23] By preference two or more of the filaments are united together before passing onto the bobbin, for which purpose two or more of the nozzles are arranged side by side.[23]

(4) Note that the mechanism used for winding in Chardonnet's process is similar to that for spinning and winding cocoon silk.

(5) Chardonnet had noticed as early as 1886 that *'the threads prepared by spinning the said filaments may be treated with a hydrometric or non-combustible preparation, and the fabric woven there from may be treated with incombustible dressing, such as a mixture of gelatine, glycerine and sugar'.*[23]

Chardonnet well recognized the difference between science and technology. He said to explain the reason why such an apparently lengthy period was required for putting the first discovery on a permanent footing[92,93]; *'The time employed over this work would appear* *to be exaggerated if one did not remember that the establishment of so new and so complex an industry necessitates a whole series of studies, discoveries, and inventions……. Note the difference existing between researches in pure science and those relating to applied science, especially when it is a question of constructing a work complete in every part. In the realm of pure science each discovery in itself extends the field of human knowledge; on the other hand when applied science is in question an isolated discovery is valueless. Every problem which arise must be completely solved. The smaller badly laid stone will bring down the edifice. Sometimes it is only after months or years of industrial practice that the best solution of a problem is found'.*

6 CONCLUSION

(1) Prior to Chardonnet new material, called cellulose nitrate, had been synthesized to give intense impact to some existing industries and also acted as catalystic nuclei of emergence of novel high technology industry. This is an example of achievements of 'second' industrial revolution, which occurred after maturation of 'first' industrial revolution.

(2) Cellulose nitrate was extensively adopted as starting material for production of artificial fibers in many 'idea' patents. Before Chardonnet's invention, almost fundamental inventions, necessary for sustainable production of artificial fibers, including synthesis of starting material, preparation of spinning solution, spinning of filaments through die, and after-treatment of the fibers, had been made separately, although at very primitive stage.

(3) Chardonnet succeeded in materialization of artificial silk by combining the essentials, already invented by others. He developed scale-up technology by establishing the detailed operating conditions, and by designing and constructing the very purposeful and precise machines.

(4) Chardonnet was the first person,
who named fibers spun from collodion or cellulose solutions 'artificial silk',
who gave detailed conditions in his patent specifications with figures,
who applied numerous patents over long years,
who applied his patents internationally,
who commercialized his inventions on large scale,
who devoted his whole life to chemical fiber industry, and
who opened 'Age of realization of technology' in chemical fibers.

Acknowledgment: The author should like to express his sincere gratitude to the late Dr. Eva Keller, UK for her help in searching reference.

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AUSGEGEBEN DEN 5. JANUAR 1887.

KAISERLICHES PATENTAMT.

PATENTSCHRIFT

— № 38368 —

5 2 87

KLASSE 29: GESPINNSTFASERN.

HILAIRE DE CHARDONNET IN BESANÇON (DOUBS, FRANKREICH).

Verfahren zur Herstellung künstlicher Seide.

Patentirt im Deutschen Reiche vom 20. December 1885 ab.

Die vorliegende Erfindung betrifft die Herstellung künstlicher Seide aus besonders zusammengesetzten Flüssigkeiten, welche in den Zustand zäher, biegsamer und glänzender Fäden übergeführt werden.

Diese Flüssigkeit ist eine Art Collodium, welche durch Auflösung von Pyroxylin, eines reducirenden Metallchlorürs und einer kleinen Quantität einer oxydirbaren organischen Base in einer Mischung von Aether und Alkohol erhalten wird.

Das Pyroxylin wird durch Nitrirung gereinigter Cellulose, welche aus Holzstoff, Strohpapierzeug, Baumwolle, Lumpen, Flieſspapier oder dergleichen hergestellt sein kann, gewonnen.

Zu dem Zwecke löst man in der Wärme 100 g Pyroxylin, 10 bis 20 g eines reducirenden Metallchlorürs, z. B. Eisen-, Chrom-, Mangan- oder Zinnchlorür, ungefähr 0,2 g einer oxydirbaren organischen Base, z. B. Chinin, Anilin, Rosanilin, in 2 bis 5 l eines Gemisches von 40 proc. Aether und 60 proc. Alkohol. Dieser Lösung setzt man noch einen löslichen Farbstoff zu.

Um eine für die vorliegenden Zwecke gute Flüssigkeit zu erhalten, löst man zunächst das Pyroxylin in dem gröſseren Theil des Gemisches von Alkohol und Aether auf und in dem kleineren Theil desselben das Metallchlorür, die organische Base und die Farbe. Die beiden Lösungen werden dann mit einander vereinigt.

Die angewendeten Mengenverhältnisse ändern sich je nach der Natur des Pyroxylins und nach der Elasticität, welche der aus der Flüssigkeit herzustellende Faden erhalten soll.

Wenn man die auf diese Weise hergestellte heiſse Flüssigkeit durch ein enges, in einer kalten Flüssigkeit, z. B. Wasser, angeordnetes Mundstück austreten läſst, so erstarrt der austretende dünne Strahl der collodiumähnlichen Flüssigkeit sofort auf seiner Auſsenfläche und bildet auf diese Weise einen festen Faden. Dieser Faden stellt sich dar als ein auſsen starres Röhrchen, welches eine innere, noch flüssige Säule umschlieſst. Man kann dann diesen Faden auſserhalb des Wassers an der Luft noch dünner ausziehen. In solchen dünnen Fäden trocknet und erhärtet die Masse dann vollständig und bildet infolge ihres Glanzes die künstliche Seide.

Der Zusatz von Farbstoff geschieht nur, um der künstlichen Seide eine bestimmte Farbe zu verleihen.

PATENT-ANSPRUCH:

Die Herstellung künstlicher Seide, darin bestehend, daſs man eine collodiumähnliche Flüssigkeit durch Auflösung von Pyroxylin, Eisen-, Chrom-, Mangan- oder Zinnchlorür, Chinin, Anilin, Rosanilin, Nicotin, Brucin, Cinchonin, Atropin, Morphin, Salicin oder Caffein in einer Mischung von Aether und Alkohol unter Zusatz eines löslichen Farbstoffes erzeugt, diese in heiſsem Zustande befindliche Flüssigkeit durch feine Röhrchen in eine kalte Erstarrungsflüssigkeit austreten läſst und den erst äuſserlich erstarrten Faden auſserhalb der Erstarrungsflüssigkeit an der Luft noch dünner auszieht, worauf die vollständige Erstarrung und Trocknung eintritt.

Photograph 1 : Front cover of Chardonnet's first invention

(Deutsche Patent Nr. 36,368) (ret. 54)